

Fluctuation theorem for entropy production during effusion of an ideal gas with momentum transfer

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We derive an exact expression for entropy production during effusion of an ideal gas driven by momentum transfer in addition to energy and particle flux. Following the treatment in Phys. Rev. E **74**, 021117 (2006), we construct a master equation formulation of the process and explicitly verify the thermodynamic fluctuation theorem, thereby directly exhibiting its extended applicability to particle flows and hence to hydrodynamic systems.

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I. INTRODUCTION

Since the pioneering work of Onsager [1] on the relation between linear response and equilibrium fluctuations, his insights have been further formalized in, for example, the theory of linear irreversible processes [2] and the fluctuation-dissipation theorem [3]. Over the past decade some new surprising results have been discovered that suggest relations valid far away from equilibrium, notably the fluctuation [4] and work [5] theorems. The fluctuation theorem, originally demonstrated for nonequilibrium steady states in thermostated systems, has been proven in a number of different settings. Basically, it states that during an experiment of duration t , it is exponentially more likely to observe a positive entropy production ΔS rather than an equally large negative one,

$$\frac{P_t(\Delta S)}{P_t(-\Delta S)} = e^{\Delta S/k}. \quad (1)$$

In the application to nonequilibrium steady states, the above result is typically only valid in the asymptotic limit $t \rightarrow \infty$ and expresses a symmetry property of large deviations.

We address another scenario in which the system is perturbed out of a state which is initially at equilibrium. The so-called transient fluctuation theorem is then valid for all times t . We consider the problem of a Knudsen flow between ideal gases that have overall non-zero momentum. In this case, the stationary state is reached instantaneously, so that there is no distinction between the transient and steady state versions of the theorem. We show that the system obeys a detailed fluctuation theorem which includes (1) as a special case. Our calculation is an extension of the one given in [6] to include momentum transfer. The interest of this extension is manifold. First, the derivation of the fluctuation theorem is somewhat more complicated since the momentum is a quantity which is odd under velocity inversion. Second, momentum, together with particle number and energy, are the

conserved quantities whose transport forms the basis of hydrodynamics. Our derivation therefore puts the fluctuation theorem fully in this context (see also [7]). Finally, as a bi-product, we calculate the Onsager matrix for the Knudsen flow problem including momentum transport.

In Sec. II we formulate the fluctuation theorem for effusion with momentum transfer for an ideal gas. Section III generalizes the derivation of the master equation and cumulant generating function in [6] to the case with momentum transfer. Verification of the fluctuation theorem is detailed in Sec. IV, and the lowest order cumulants are exhibited in Sec. V. We use these results to verify the Onsager relations for this nonequilibrium system in Sec. VI. We end with a brief conclusion in Sec. VII. Some details of the calculations are presented in appendices.

II. FLUCTUATION THEOREM FOR EFFUSION WITH MOMENTUM TRANSFER

We begin by considering two (infinitely) large neighboring reservoirs, A and B , each of which contains an ideal gas of uniform density n_i in equilibrium at temperature T_i , $i \in A, B$. In addition, the particles of gas i have an overall center of mass velocity V_i in the \mathbf{e}_x direction (Fig. 1). That is, the velocity distributions of the gas particles take the Maxwellian form

$$\phi_i = \left(\frac{m}{2\pi k T_i} \right)^{3/2} \exp \left(-\frac{m(\mathbf{v} - V_i \mathbf{e}_x)^2}{2k T_i} \right). \quad (2)$$

The two reservoirs are separated by a common adiabatic wall parallel to the \mathbf{e}_x direction, with a hole of surface area σ whose linear dimensions are small compared with the mean free path of the particles. As a result, the local equilibrium in each reservoir is not disturbed by the exchange of mass, heat, and momentum during a finite time interval t in which the hole is open. Upon a transfer of total energy ΔU , particles ΔN , and momentum Δp_x during this time interval, the overall change in entropy

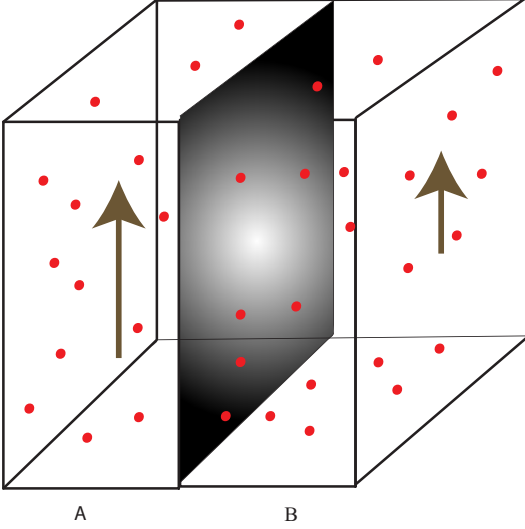


FIG. 1: The ideal gas in compartment A is characterized by temperature T_A , number density n_A , and flow velocity V_A . Similarly, the ideal gas in compartment B is characterized by temperature T_B , number density n_B , and flow velocity V_B . Velocities V_A and V_B are represented by the vertical arrows within each compartment and are taken to be parallel to the adiabatic wall separating the two gases.

for the system is given by

$$\begin{aligned}\Delta S &= \Delta S_A + \Delta S_B \\ &= -\frac{1}{T_A}\Delta U + \left(\frac{\mu_A}{T_A} - \frac{mV_A^2}{2T_A}\right)\Delta N + \frac{V_A}{T_A}\Delta p_x \\ &\quad + \frac{1}{T_B}\Delta U - \left(\frac{\mu_B}{T_B} - \frac{mV_B^2}{2T_B}\right)\Delta N - \frac{V_B}{T_B}\Delta p_x \\ &= \mathcal{A}_U\Delta U + \mathcal{A}_N\Delta N + \mathcal{A}_{p_x}\Delta p_x,\end{aligned}\quad (3)$$

where we have introduced the thermodynamic forces for energy, particle, and momentum transfer [8]:

$$\begin{aligned}\mathcal{A}_U &= \frac{1}{T_B} - \frac{1}{T_A}, \\ \mathcal{A}_N &= \frac{\mu_A}{T_A} - \frac{mV_A^2}{2T_A} - \left(\frac{\mu_B}{T_B} - \frac{mV_B^2}{2T_B}\right) \\ &= k \log \left[\frac{n_A}{n_B} \left(\frac{T_B}{T_A} \right)^{\frac{3}{2}} \right] + \left(\frac{mV_B^2}{2T_B} - \frac{mV_A^2}{2T_A} \right), \\ \mathcal{A}_{p_x} &= \frac{V_A}{T_A} - \frac{V_B}{T_B}.\end{aligned}\quad (4)$$

In the equation for \mathcal{A}_N , we have used the expression for the chemical potential μ of an ideal gas at rest. Since the explicit expression for the thermodynamic forces in systems with momentum is not readily available, we provide a brief derivation in Appendix A.

The variables ΔU , ΔN , and Δp_x all correspond to fluctuating quantities influenced by single particle crossings on each side of the adiabatic wall. As a result, the total entropy production ΔS , which will be observed during

the time duration t , is likewise a fluctuating quantity. However, time reversal symmetry of the microscopic dynamics a relation for the probability distribution of this entropy production, as expressed in Eq. (1). Due to the absence of memory effects, ΔS is in fact a stochastic process with independent increments: contributions to ΔS from any two equal, non-overlapping time intervals are independent identically distributed random variables. It is therefore convenient to introduce the cumulant generating function, which takes the form

$$\langle e^{-\lambda \Delta S} \rangle = e^{-tg(\lambda)}. \quad (5)$$

The fluctuation theorem, Eq. 1, implies the following symmetry property:

$$g(\lambda) = g(k^{-1} - \lambda). \quad (6)$$

As the derivation in Appendix B points out, one can augment the observation of the entropy production with additional variables, while retaining the form of the fluctuation theorem. Hence the following more detailed fluctuation theorem, which is expressed in terms of the joint probability density involving all three conserved quantities, particle number, momentum and energy, is obtained:

$$\frac{P_t(\Delta U, \Delta N, \Delta p_x)}{P_t(-\Delta U, -\Delta N, -\Delta p_x)} = e^{\Delta S/k}. \quad (7)$$

Since the increments of ΔU , ΔN , and Δp_x are also independent, we can write the corresponding cumulant generating function as

$$\langle e^{-(\lambda_U \Delta U + \lambda_N \Delta N + \lambda_{p_x} \Delta p_x)} \rangle = e^{-tg(\lambda_U, \lambda_N, \lambda_{p_x})}. \quad (8)$$

The detailed fluctuation theorem then requires the following symmetry relation, similar to Eq. (6):

$$\begin{aligned}g(\lambda_U, \lambda_N, \lambda_{p_x}) \\ = g(\mathcal{A}_U k^{-1} - \lambda_U, \mathcal{A}_N k^{-1} - \lambda_N, \mathcal{A}_{p_x} k^{-1} - \lambda_{p_x}).\end{aligned}\quad (9)$$

Note finally that Eq. (7), apart from implying the normal fluctuation theorem Eq. (1), also implies fluctuation theorems for particle, energy, and momentum transfer individually when the complementary thermodynamic forces are zero:

$$\begin{aligned}\frac{\mathcal{P}_t(\Delta U)}{\mathcal{P}_t(-\Delta U)} &= e^{\Delta S/k}; \quad \mathcal{A}_N = \mathcal{A}_{p_x} = 0, \\ \frac{\mathcal{P}_t(\Delta N)}{\mathcal{P}_t(-\Delta N)} &= e^{\Delta S/k}; \quad \mathcal{A}_U = \mathcal{A}_{p_x} = 0, \\ \frac{\mathcal{P}_t(\Delta p_x)}{\mathcal{P}_t(-\Delta p_x)} &= e^{\Delta S/k}; \quad \mathcal{A}_U = \mathcal{A}_N = 0.\end{aligned}\quad (10)$$

III. MASTER EQUATION AND CUMULANT GENERATING FUNCTION

If we choose a sufficiently small time interval dt , the contributions to the quantities ΔU , ΔN , and Δp_x arise

from individual particles crossing the hole. The kinetic theory of gases allows us to calculate the probability per unit time, $T_{i \rightarrow j}(E, p_x)$, to observe a particle with kinetic energy $E = \frac{1}{2}mv^2$ and momentum $p_x = mv_x$ crossing the hole from reservoir i to reservoir j . Specifically, the transition rate in question is given by (see Appendix A):

$$T_{i \rightarrow j}(E, p_x) = \frac{\sigma n_i}{m(k\pi T_i)^{3/2}} \left(E - \frac{p_x^2}{2m}\right)^{1/2} \times \exp \left[-\frac{m}{2kT_i} \left(\frac{2(E - \frac{p_x^2}{2m})}{m} + \left(\frac{p_x}{m} + V_i\right)^2 \right) \right], \quad (11)$$

with $(i, j) = (A, B)$ or $(i, j) = (B, A)$. Hence, the probability density $P_t(\Delta U, \Delta N, \Delta p_x)$ obeys the master equation

$$\begin{aligned} \partial_t P_t(\Delta U, \Delta N, \Delta p_x) &= \int_{-\infty}^{\infty} dp_x \int_{p_x^2/2m}^{\infty} dE T_{A \rightarrow B} \\ &\quad \times P_t(\Delta U - E, \Delta N - 1, \Delta p_x - p_x) \\ &+ \int_{-\infty}^{\infty} dp_x \int_{p_x^2/2m}^{\infty} dE T_{B \rightarrow A} \\ &\quad \times P_t(\Delta U + E, \Delta N + 1, \Delta p_x + p_x) \\ &- P_t(\Delta U, \Delta N, \Delta p_x) \int_{-\infty}^{\infty} dp_x \int_{p_x^2/2m}^{\infty} dE \\ &\quad \times (T_{A \rightarrow B} + T_{B \rightarrow A}). \end{aligned} \quad (12)$$

We have written $T_{i \rightarrow j}(E, p_x)$ without the arguments for economy of notation. We can take advantage of the convolution structure of the integral operators by considering the equation in Fourier space; that is, we multiply both sides of the equation by $\exp[-(\lambda_U \Delta U + \lambda_N \Delta N + \lambda_{p_x} \Delta p_x)]$ and integrate $\Delta U, \Delta p_x$ over all space and sum over all integers ΔN . We arrive at the expression

$$\begin{aligned} \partial_t \tilde{P}(\lambda_U, \lambda_N, \lambda_{p_x}) &= \tilde{P}(\lambda_U, \lambda_N, \lambda_{p_x}) I_1 \\ &+ \tilde{P}(\lambda_U, \lambda_N, \lambda_{p_x}) I_2 - \tilde{P}(\lambda_U, \lambda_N, \lambda_{p_x}) I_3, \end{aligned} \quad (13)$$

where

$$\begin{aligned} I_1 &= e^{-\lambda_N} \int_{-\infty}^{\infty} dp_x \int_{p_x^2/2m}^{\infty} dE T_{A \rightarrow B} e^{-(\lambda_U E + \lambda_{p_x} p_x)}, \\ I_2 &= e^{\lambda_N} \int_{-\infty}^{\infty} dp_x \int_{p_x^2/2m}^{\infty} dE T_{B \rightarrow A} e^{(\lambda_U E + \lambda_{p_x} p_x)}, \\ I_3 &= \int_{-\infty}^{\infty} dp_x \int_{p_x^2/2m}^{\infty} dE (T_{A \rightarrow B} + T_{B \rightarrow A}). \end{aligned} \quad (14)$$

From this expression we can write $g(\lambda_U, \lambda_N, \lambda_{p_x})$, defined in Eq. (8), as

$$g(\lambda_U, \lambda_N, \lambda_{p_x}) = I_3 - (I_1 + I_2). \quad (15)$$

The integrals (14) can easily be performed by switching to the variable $z = E - p_x^2/2m$ and integrating z from zero

to infinity and p_x over all space, as before. We thereby arrive at our final expression for $g(\lambda_U, \lambda_N, \lambda_{p_x})$:

$$\begin{aligned} g(\lambda_U, \lambda_N, \lambda_{p_x}) &= \sigma \left(\frac{k}{2\pi m} \right)^{1/2} \\ &\quad \times \left[n_A T_A^{1/2} \left(1 - \frac{G_A}{(1 + kT_A \lambda_U)^2} \right) \right. \\ &\quad \left. + n_B T_B^{1/2} \left(1 - \frac{G_B}{(1 - kT_B \lambda_U)^2} \right) \right], \end{aligned} \quad (16)$$

where

$$\begin{aligned} G_A &\equiv \exp \left(-\lambda_N - \frac{mV_A^2 \lambda_U - kmT_A \lambda_{p_x}^2 + 2mV_A \lambda_{p_x}}{2(1 + kT_A \lambda_U)} \right), \\ G_B &\equiv \exp \left(\lambda_N + \frac{mV_B^2 \lambda_U + kmT_B \lambda_{p_x}^2 + 2mV_B \lambda_{p_x}}{2(1 - kT_B \lambda_U)} \right). \end{aligned} \quad (17)$$

Notice that $g(\lambda_U, \lambda_N, \lambda_{p_x})$ can be written as a sum of two contributions,

$$g(\lambda_U, \lambda_N, \lambda_{p_x}) = g_A(\lambda_U, \lambda_N, \lambda_{p_x}) + g_B(\lambda_U, \lambda_N, \lambda_{p_x}), \quad (18)$$

with

$$\begin{aligned} g_A(\lambda_U, \lambda_N, \lambda_{p_x}) &= \sigma \left(\frac{k}{2\pi m} \right)^{1/2} \\ &\quad \times n_A T_A^{1/2} \left(1 - \frac{G_A}{(1 + kT_A \lambda_U)^2} \right), \\ g_B(\lambda_U, \lambda_N, \lambda_{p_x}) &= \sigma \left(\frac{k}{2\pi m} \right)^{1/2} \\ &\quad \times n_B T_B^{1/2} \left(1 - \frac{G_B}{(1 - kT_B \lambda_U)^2} \right). \end{aligned} \quad (19)$$

This additivity property arises from the statistical independence of the fluxes from $A \rightarrow B$ and $B \rightarrow A$.

IV. FLUCTUATION SYMMETRY

We now proceed to explicitly verify the symmetry relation (9) and hence the fluctuation theorem. Conceptually, one may understand this symmetry relation as follows. Under the symmetry operation \mathcal{T} – that is, under the transformation given by the r.h.s. of Eq. (9) – the term containing the exponential in g_A (which we call $g_{A,1}$) becomes the corresponding term from g_B (which we call $g_{B,1}$) and similarly, the original $g_{B,1}$ term becomes $g_{A,1}$, thereby preserving the overall structure of g . Mathematically, we can express this as:

$$\begin{aligned} \mathcal{T}[g_{A,1}] &= g_{B,1}, \\ \mathcal{T}[g_{B,1}] &= g_{A,1}, \end{aligned} \quad (20)$$

where

$$g_{A,1} = \sigma (k2\pi m)^{1/2} n_A T_A^{1/2} (1 + kT_A \lambda_U)^{-2} G_A, \quad (21)$$

and

$$g_{B,1} = \sigma (k2\pi m)^{1/2} n_B T_B^{1/2} (1 - kT_B \lambda_U)^{-2} G_B. \quad (22)$$

Explicitly, we have

$$\begin{aligned} \mathcal{T}[g_{A,1}] &= \sigma \left(\frac{k}{2\pi m} \right)^{1/2} n_A T_A^{1/2} (1 + kT_A \Lambda_U)^{-2} \\ &\times \exp \left\{ \log \left[\frac{n_A}{n_B} \left(\frac{T_B}{T_A} \right)^{3/2} \right] + \Lambda_N \right\} \\ &\times \exp \left[\frac{-mV_A^2 \Lambda_U + kmT_A \Lambda_{p_x}^2}{2(1 + kT_A \Lambda_U)} \right] \\ &\times \exp \left(\frac{-2mV_A \lambda_{p_x}}{2(1 + kT_A \Lambda_U)} \right) \\ &= \sigma \left(\frac{k}{2\pi m} \right)^{1/2} n_A T_A^{1/2} \Lambda^{-2} \left(\frac{n_A}{n_B} \frac{T_B}{T_A} \right) \\ &\times \exp \left[-\lambda_N + \frac{2\Lambda \left(\frac{V_B^2 m}{2kT_B} - \frac{V_A^2 m}{2kT_A} \right) - mV_A^2 \Lambda_U}{2\Lambda} \right] \\ &\times \exp \left(\frac{kmT_A \Lambda_{p_x}^2 - 2mV_A \lambda_{p_x}}{2\Lambda} \right), \end{aligned} \quad (23)$$

where

$$\begin{aligned} \Lambda_U &\equiv \frac{1}{kT_B} - \frac{1}{kT_A} - \lambda_U, \\ \Lambda_{p_x} &\equiv \frac{V_A}{kT_A} - \frac{V_B}{kT_B} - \lambda_{p_x}, \\ \Lambda_N &\equiv \frac{V_B^2 m}{2kT_B} - \frac{V_A^2 m}{2kT_A} - \lambda_N, \\ \Lambda &\equiv \frac{T_A}{T_B} (1 - kT_B \lambda_U). \end{aligned} \quad (24)$$

Following simplification, this reduces to $g_{B,1}$. A similar result holds for $\mathcal{T}[g_{B,1}]$, and therefore the fluctuation theorem symmetry is satisfied.

V. CUMULANTS

The joint cumulant κ_{ijk} of power i in energy flux, j in particle flux, and k in momentum flux appears as a coefficient in the Taylor expansion of the cumulant generating function, namely,

$$g_A(\lambda_U, \lambda_N, \lambda_{p_x}) = -\frac{1}{t} \sum_{i,j,k=0}^{\infty} \frac{(-1)^{i+j+k} \lambda_U^i \lambda_N^j \lambda_{p_x}^k}{i!j!k!} \kappa_{ijk}. \quad (25)$$

While our expression for $g_A(\lambda_U, \lambda_N, \lambda_{p_x})$ allows us to calculate joint cumulants of any order, we here mention only the first order results, which are relevant for verifying the

Onsager relations in the subsequent section:

$$\begin{aligned} \kappa_{100} &= \langle \Delta U \rangle \\ &= t\sigma \left(\frac{k}{2\pi m} \right)^{1/2} \left(n_A T_A^{1/2} (2kT_A + \frac{mV_A^2}{2}) \right. \\ &\quad \left. - n_B T_B^{1/2} (2kT_B + \frac{mV_B^2}{2}) \right), \\ \kappa_{010} &= \langle \Delta N \rangle \\ &= t\sigma \left(\frac{k}{2\pi m} \right)^{1/2} (n_A T_A^{1/2} - n_B T_B^{1/2}), \\ \kappa_{001} &= \langle \Delta p_x \rangle \\ &= t\sigma \left(\frac{km}{2\pi} \right)^{1/2} (n_A V_A T_A^{1/2} - n_B V_B T_B^{1/2}). \end{aligned} \quad (26)$$

Note that the cumulant associated with energy $\langle \Delta U \rangle$ contains terms corresponding to both particle transport and momentum transport.

VI. ONSAGER RELATIONS

Averaging Eq. (3) and taking the time derivative leads us to an equation for the average entropy production,

$$\frac{d}{dt} \langle \Delta S \rangle = \mathcal{J}_U \mathcal{A}_U + \mathcal{J}_N \mathcal{A}_N + \mathcal{J}_{p_x} \mathcal{A}_{p_x}, \quad (27)$$

with the macroscopic fluxes \mathcal{J}_X defined as

$$\begin{aligned} \mathcal{J}_U &= \frac{d}{dt} \langle \Delta U \rangle \\ &= \sigma \left(\frac{k}{2\pi m} \right)^{1/2} \left(n_A T_A^{1/2} (2kT_A + \frac{mV_A^2}{2}) \right. \\ &\quad \left. - n_B T_B^{1/2} (2kT_B + \frac{mV_B^2}{2}) \right), \\ \mathcal{J}_N &= \frac{d}{dt} \langle \Delta N \rangle = \sigma \left(\frac{k}{2\pi m} \right)^{1/2} (n_A T_A^{1/2} - n_B T_B^{1/2}), \\ \mathcal{J}_{p_x} &= \frac{d}{dt} \langle \Delta p_x \rangle \\ &= \sigma \left(\frac{km}{2\pi} \right)^{1/2} (n_A V_A T_A^{1/2} - n_B V_B T_B^{1/2}). \end{aligned} \quad (28)$$

While these fluxes are in general complicated nonlinear functions of the affinities $(\mathcal{A}_U, \mathcal{A}_N, \mathcal{A}_{p_x})$, near equilibrium we can write:

$$\begin{aligned} T_A &= T - \frac{\Delta T}{2}, & T_B &= T + \frac{\Delta T}{2}, \\ n_A &= n - \frac{\Delta n}{2}, & n_B &= n + \frac{\Delta n}{2}, \\ V_A &= V - \frac{\Delta V}{2}, & V_B &= V + \frac{\Delta V}{2}, \end{aligned} \quad (29)$$

and expand the forces and fluxes to first order in the small deviations ΔT , Δn , and ΔV . To linear order, the

thermodynamic forces become

$$\begin{aligned}\mathcal{A}_U &= -\frac{\Delta T}{T^2}; \\ \mathcal{A}_N &= \frac{mV}{T}\Delta V + \left(\frac{3k}{2T} - \frac{mV^2}{2T^2}\right)\Delta T - \frac{k}{n}\Delta n \\ \mathcal{A}_{p_x} &= -\frac{\Delta V}{T} + \frac{V}{T^2}\Delta T.\end{aligned}\quad (30)$$

Taylor expansions of the fluxes $\mathcal{J}_U, \mathcal{J}_N$, and \mathcal{J}_{p_x} [Eq. (28)] allow us to write

$$\bar{\mathcal{J}} = \mathbf{O}\bar{\mathcal{A}}, \quad (31)$$

where $\bar{\mathcal{J}} = (\mathcal{J}_U, \mathcal{J}_N, \mathcal{J}_{p_x})^T$ and $\bar{\mathcal{A}} = (\mathcal{A}_U, \mathcal{A}_N, \mathcal{A}_{p_x})^T$. The Onsager matrix \mathbf{O} is given by:

$$\mathbf{O} = \sigma \left(\frac{k}{2\pi m} \right)^{1/2} n T^{3/2} \begin{pmatrix} 6kT + 3mV^2 + \frac{(mV^2)^2}{4kT} & 2 + \frac{mV^2}{2kT} & \frac{1}{2}mV(6 + \frac{mV^2}{kT}) \\ 2 + \frac{mV^2}{2kT} & \frac{1}{kT} & \frac{mV}{kT} \\ \frac{1}{2}mV(6 + \frac{mV^2}{kT}) & \frac{mV}{kT} & m + \frac{(mV)^2}{kT} \end{pmatrix}, \quad (32)$$

which clearly has the required symmetry $O_{ij} = O_{ji}$. The Onsager relations [Eq. (31)] fully detail the complex coupling between energy, particle, and momentum transport in the linear regime.

Note that in the case of moving gases, $V \neq 0$, the presence of a temperature gradient alone ($\Delta n = \Delta V = 0$) is sufficient to produce a nonzero net flux of momentum. Note also that when there is only a momentum gradient, $\Delta T = \Delta n = 0$, the heat, particle, and momentum fluxes reduce to:

$$\begin{aligned}\mathcal{J}_U &= -\frac{\sigma k^{\frac{1}{2}} n T^{\frac{1}{2}}}{(2\pi m)^{\frac{1}{2}}} (mV) \Delta V, \\ \mathcal{J}_N &= 0, \\ \mathcal{J}_p &= -\frac{\sigma k^{\frac{1}{2}} n T^{\frac{1}{2}}}{(2\pi m)^{\frac{1}{2}}} m \Delta V.\end{aligned}\quad (33)$$

Therefore, when we choose the velocities to be equal but opposite so that $V = 0$, the only nonzero flux is due to momentum transport. In other words, momentum exchange takes place without a net exchange of particles or energy.

VII. CONCLUSION

The work and fluctuation theorems are quite remarkable. They are basically one further step in Onsager's program to take into account the time-reversal symmetry of the microscopic dynamics. This results in a stringent constraint on the probability density of the entropy production. The implications of this result are still being

explored. In this paper we have shown by an explicit microscopically exact calculation that the fluctuation theorem applies for the effusion between ideal gases with non-zero overall momentum. This sets the stage for the application of the formalism in fluctuating hydrodynamics.

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APPENDIX A

We can derive the thermodynamic forces for an ideal gas of N particles in volume \mathcal{V} with non-zero momentum by considering the entropy $S(U, N, \mathcal{V})$ of a gas at rest as a function of U , the total energy, N , and \mathcal{V} . Because adding an overall velocity to the gas does not change its volume in phase space and hence its entropy, we can write the entropy $S(U, N, \mathcal{V}, p)$ of a flowing gas which depends on momentum p in terms of the entropy $S_0(U, N, \mathcal{V})$ of a gas at rest:

$$S(U, N, \mathcal{V}, p) = S_0\left(\left(U - \frac{p^2}{2Nm}\right), N, \mathcal{V}\right) = S_0(\epsilon, N, \mathcal{V}), \quad (A1)$$

where $\epsilon \equiv U - p^2/2Nm$ represents the internal energy of the gas. The Sackur-Tetrode formula [9] provides the explicit expression for $S(\epsilon, N, \mathcal{V})$ which, with Eq. (A1)

leads to

$$S = kN \log \left[\frac{\mathcal{V}}{N} \left(\frac{U - \frac{p^2}{2mN}}{N} \right)^{3/2} \right] + \frac{3}{2} kN \left[\frac{5}{3} + \log \left(\frac{4\pi m}{3h^2} \right) \right]. \quad (\text{A2})$$

Here h is Planck's constant and m is the mass of a single gas particle. We can write the total entropy change of the effusion process considered here as

$$\begin{aligned} dS &= \frac{\partial S_A}{\partial U_A} dU_A + \frac{\partial S_A}{\partial N_A} dN_A + \frac{\partial S_A}{\partial p_A} dp_A \\ &+ \frac{\partial S_B}{\partial U_B} dU_B + \frac{\partial S_B}{\partial N_B} dN_B + \frac{\partial S_B}{\partial p_B} dp_B \\ &= dU \left(\frac{\partial S_B}{\partial U_B} - \frac{\partial S_A}{\partial U_A} \right) + dN \left(\frac{\partial S_B}{\partial N_B} - \frac{\partial S_A}{\partial N_A} \right) \\ &+ dp \left(\frac{\partial S_B}{\partial p_B} - \frac{\partial S_A}{\partial p_A} \right), \end{aligned} \quad (\text{A3})$$

where S_i corresponds to Eq. (A2) with $U \rightarrow U_i$, $N \rightarrow N_i$, and $p \rightarrow p_i$, $i \in A, B$, and we have used momentum, energy, and particle conservation to write $dU = -dU_A = dU_B$, $dN = -dN_A = dN_B$, and $dp = -dp_A = dp_B$. Performing the above calculations and considering that the total energy U of an ideal gas with overall momentum p at temperature T is given by

$$U = \frac{3N}{2kT} + \frac{p^2}{2m}, \quad (\text{A4})$$

we arrive after simplification at the expressions given in Eq. (4).

APPENDIX B

We give a derivation of the fluctuation theorem, Eq. (7), by adapting to the present case the procedure introduced in [10]. We consider the Hamiltonian evolution of a system, consisting of two disjoint subsystems A and B initially at equilibrium characterized by micro-canonical distributions with total particle number, momentum, energy and volume equal to N_i , p_i , U_i and \mathcal{V}_i , $i = A, B$, respectively. At the initial time, the constraint separating both systems is broken. It is assumed that this can be achieved without any external work, momentum exchange or other perturbation of the subsystems. This is clearly the case for the opening of a hole in the adiabatic wall separating ideal gases, as considered here. After a time interval of duration t , the constraint is again introduced at no cost of energy or momentum. One records the new values of the parameters N'_i , p'_i and U'_i . The amounts $(\Delta N, \Delta p, \Delta U)$ that are transported from system A to system B will depend on the specific run, i.e., on the starting configuration at $t = 0$. Let the volume in phase space corresponding to the initial states that lead to the transport of these amounts be denoted by $\Omega_{(N_i, p_i, U_i)}(\Delta N, \Delta p, \Delta U)$. The probability to observe

such a realization is then given by

$$P_{(N_i, p_i, U_i)}(\Delta N, \Delta p, \Delta U) = \frac{\Omega_{(N_i, p_i, U_i)}(\Delta N, \Delta p, \Delta U)}{\Omega_{(N_i, p_i, U_i)}}, \quad (\text{B1})$$

where $\Omega_{(N_i, p_i, U_i)}$ is the total phase space volume. We now apply this very same result for parameter values N'_i , $-p'_i$ and U'_i , $i = A, B$, and consider the probability of transporting the amounts $(-\Delta N, \Delta p, -\Delta U)$. Apart from velocity inversion, the final values in this procedure are then the initial ones of the first scenario, i.e., $(N_i, -p_i, U_i)$. The corresponding probability reads

$$\begin{aligned} P_{(N'_i, -p'_i, U'_i)}(-\Delta N, \Delta p, -\Delta U) \\ = \frac{\Omega_{(N'_i, -p'_i, U'_i)}(-\Delta N, \Delta p, -\Delta U)}{\Omega_{(N'_i, -p'_i, U'_i)}}. \end{aligned} \quad (\text{B2})$$

By micro-reversibility, there is a one-to-one correspondence between each trajectory in the first situation with the time reversed trajectory in the second situation. Furthermore, since Hamiltonian dynamics preserves phase volume, the numerators in the r.h.s. of Eqs. (B1) and (B2) are identical. We conclude that

$$\begin{aligned} \frac{P_{(N_i, p_i, U_i)}(\Delta N, \Delta p, \Delta U)}{P_{(N'_i, -p'_i, U'_i)}(-\Delta N, \Delta p, -\Delta U)} &= \frac{\Omega_{(N'_i, -p'_i, U'_i)}}{\Omega_{(N_i, p_i, U_i)}} \\ &= \exp\left(\frac{\Delta S}{k_B}\right), \end{aligned} \quad (\text{B3})$$

where we used the fact that the entropy of a state is Boltzmann's constant times the logarithm of the phase space volume Ω of that state. ΔS is thus the entropy difference between states with and without the primes. We now note that inverting the momenta of the gases does not change the statistics of particle and energy transport, but will obviously change the sign of the momentum transfer, $P_{(N'_i, -p'_i, U'_i)}(-\Delta N, \Delta p, -\Delta U) = P_{(N'_i, p'_i, U'_i)}(-\Delta N, -\Delta p, -\Delta U)$. Hence we can rewrite Eq. (B3) as follows:

$$\frac{P_{(N_i, p_i, U_i)}(\Delta N, \Delta p, \Delta U)}{P_{(N'_i, p'_i, U'_i)}(-\Delta N, -\Delta p, -\Delta U)} = \exp\left(\frac{\Delta S}{k}\right) \quad (\text{B4})$$

Finally, we consider the thermodynamic limit of infinitely large systems with finite particle density $n_i = N_i/\mathcal{V}_i$, momentum density $mV_i = p_i/N_i$, and energy density $u_i = U_i/\mathcal{V}_i$. We furthermore assume that the effects of the removal of the constraint do not scale with the volume, so that during the finite time t it results in non-extensive changes in the parameter values. Hence we can drop the sub-indices of P on the l.h.s. of Eq. (B4). Adding the sub-index t to emphasize the duration of the exchange, one can thus rewrite Eq. (B4) as Eq. (7) of the main text.

APPENDIX C

Here we briefly derive the formula for the transition rate $T_{A \rightarrow B}(E, p_x)$ using the kinetic theory of gases. We

consider the \hat{z} direction to point from reservoir A to reservoir B . We require $T_{A \rightarrow B}(E, p_x) dE dp_x dt$, the probability to observe a particle with kinetic energy in the range $(E, E + dE)$ and momentum in the range $(p_x, p_x + dp_x)$ to cross the hole from A to B in a time interval dt . The z component of the position of a particle with velocity \mathbf{v} must be located within a cylinder of base area σ (the area of the hole) and height $v_z dt$ measured from the wall. Furthermore, it must be traveling in the $+\mathbf{e}_z$ direction (towards the hole). The appropriate expression is

$$T_{A \rightarrow B}(E, p_x) = \int_{-\infty}^{\infty} dv_x \int_{-\infty}^{\infty} dv_y \int_0^{\infty} dv_z \sigma v_z n_A \phi_A(\mathbf{v}, V_A) \times \delta\left(\frac{mv^2}{2} - E\right) \delta(mv_x - p_x), \quad (\text{C1})$$

where $\phi_A(\mathbf{v}, V_A)$ is the Maxwellian given by Eq. (2), and we have explicitly noted its dependence on \mathbf{v} and V_A . A similar equation holds for $T_{A \rightarrow B}$. The v_x integral is trivial because of the second delta function, and the remaining integrals can be easily performed by changing to polar coordinates (R, θ) , given by

$$R^2 = v_y^2 + v_z^2; \quad \tan \theta = \frac{v_y}{v_z}. \quad (\text{C2})$$

This yields the expressions given in Eq. (11).

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